

Orthorhombic-to-Monoclinic Phase Transition of Ta_2NiSe_5 Induced by the Bose-Einstein Condensation of Excitons

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Using the band structure calculation and mean-field analysis of the derived three-chain Hubbard model with phonon degrees of freedom, we discuss the origin of the orthorhombic-to-monoclinic phase transition of the layered chalcogenide Ta_2NiSe_5 . We show that the Bose-Einstein condensation of excitonic electron-hole pairs cooperatively induces the instability of the phonon mode at momentum $q \rightarrow 0$ in the quasi-one-dimensional Ta-NiSe-Ta chain, resulting in the structural phase transition of the system. The calculated single-particle spectra reproduce the deformation of the band structure observed in the angle-resolved photoemission spectroscopy experiment.

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The electron-hole pair condensation in thermal equilibrium into the excitonic insulator (EI) state has attracted renewed interest in recent years because of the discoveries of a number of new materials. The idea of EI was proposed about half a century ago [1, 2], where the EI state was predicted to be realized either in a semiconductor with a small band gap or in a semimetal with a small band overlap. The formation of excitons is driven by poorly screened Coulomb interaction between conduction-band electrons and valence-band holes under condition of a low carrier concentration. If the binding energy of excitons is larger than the band gap, they may spontaneously condense at low temperatures and drive the system into a new ground state with exotic properties. This new state, which is a condensed state of a macroscopic number of excitons acquiring quantum phase coherence, is called EI [3, 4]. It has been pointed out that the semimetal-EI transition may be described in analogy with the BCS theory of superconductivity and the semiconductor-EI transition is discussed in terms of a Bose-Einstein condensation (BEC) of preformed excitons [5–9].

An example of materials for possible realization of EI is $\text{Tm}(\text{Se}, \text{Te})$, where it has been claimed that a transition into EI occurs by applying pressure [10–12] and that the superfluidity of condensed excitons is responsible for the observed anomalous properties [13]. Another promising candidate for EI is CaB_6 [14], where the observed weak ferromagnetism with an unexpectedly high Curie temperature was interpreted in terms of a doped EI [15, 16]. Also known as a candidate for EI is TiSe_2 , where the observed charge-density-wave state was interpreted to be of an excitonic type [17–19]. The spin-density-wave state of the iron-pnictide superconductors has also been argued to be of the excitonic type [20–22]. Semiconductor bilayer systems have attracted attention as well in relation to the BEC of excitons [23].

Recently, a transition-metal chalcogenide Ta_2NiSe_5 has been studied in this respect [24, 25]. This mate-

rial has a layered structure stacked loosely by a weak van der Waals interaction, and in each layer, Ni single chains and Ta double chains are running along the a -axis of the lattice to form a quasi-one-dimensional (1D) chain structure [26]. The observed resistivity shows a semiconducting behavior over a wide temperature range with a quasi-1D anisotropic electron conduction at high temperatures [27]. Then, an anomaly in the resistivity appears at 328K, which is associated with a second-order-like structural phase transition from orthorhombic to monoclinic phase [27]. The magnetic susceptibility exhibits diamagnetism in a wide temperature range (4.2 – 900 K) and shows a sudden drop (being more negative) below the structural transition temperature (328 K) [27]. The system was thus suggested to be a small band-gap semiconductor with oxidation states of Ni^{0+} ($3d^{10}$) and Ta^{5+} ($5d^0$), rather than a magnetic or Mott insulator [27, 28]. However, a recent X-ray photoemission spectroscopy (XPS) experiment, together with a cluster-model calculation, showed that Ni ions have a $3d^9\bar{L}$ character (\bar{L} is a Se $4p$ hole) and consequently Ta ions have a $5d^1$ character [24]. Moreover, the angle-resolved photoemission spectroscopy (ARPES) experiment [24, 25] showed that the spectra are strongly temperature dependent, i.e., at 40 K the flatness of the top of the valence band is extremely enhanced and the size of the band gap becomes wider. It was thereby suggested that the EI state is realized as the ground state of this material, where the spin-singlet excitons between the Ni $3d$ -Se $4p$ holes and Ta $5d$ electrons are presumed [24].

In this paper, motivated by such developments in the field, we make a theory to elucidate the origin of the structural phase transition and associated anomalous electronic properties of Ta_2NiSe_5 . We first carry out the density-functional-theory (DFT) based electronic structure calculations for the orthorhombic phase of Ta_2NiSe_5 and find that the system is a direct-gap semiconductor with the gap minimum at the Γ -point of the Brillouin zone and has a simple band structure near the Fermi

level. No hybridization occurs between the top of the valence band and bottom of the conduction band. Based on the results, we construct an effective three-chain Hubbard model to reproduce the three bands near the Fermi level. We then introduce the phonon degrees of freedom into the model and analyze it by the mean-field approximation. We calculate the ground-state and finite-temperature phase diagrams of the model to clarify the origin of the structural phase transition. The single-particle excitation spectra are also calculated.

We thus show that the BEC of excitonic electron-hole pairs cooperatively induces the instability of the phonon mode at momentum $q \rightarrow 0$ in the quasi-1D Ta-NiSe-Ta chain, resulting in the structural phase transition of the system. The spontaneous hybridization between the conduction and valence bands well explains the valence states of Ni and Ta ions observed in the XPS experiment [24] and also the calculated single-particle spectra well reproduce the deformation in the band structure near the Fermi level observed in the ARPES experiment [24, 25]. Our results thus demonstrate a possible realization of the EI state in the simplest quasi-1D electronic system of the recently corroborated material Ta_2NiSe_5 and will encourage further experimental studies of this intriguing material.

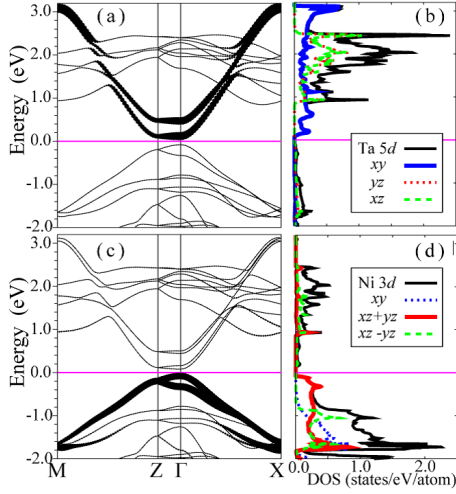


FIG. 1: (Color online) Calculated band dispersions and PDOS of the orthorhombic phase of Ta_2NiSe_5 . In (a), the width of the curves is in proportion to the weight of the Ta $5d_{xy}$ orbital, in (b), the contribution from the Ta $5d_{t_{2g}}$ orbitals is shown, in (c), the width of the curves is in proportion to the weight of the Ni $3d_{xz+yz}$ orbital, and in (d), the contribution from the Ni $3d_{t_2}$ orbitals is shown. The Fermi level is indicated by a horizontal line. The local coordinate system defined in Ref. 24 is used.

We make the band structure calculations employing the code WIEN2k [29] based on the full-potential linearized augmented-plane-wave method, where we use the generalized gradient approximation for electron correla-

tions with the exchange-correlation potential of Ref. 30. Because the crystal structure of the high-temperature orthorhombic phase of Ta_2NiSe_5 is not known, we make the structural optimization, keeping the orthorhombic structure (space group $Cmcm$) and lattice constants [26], and obtain the optimized internal coordinates of all the ions [31]. The calculated results for the band structure, however, predict a metallic state with a small band overlap and are not consistent with experiment. This may be due to a well-known problem of DFT-based band calculations, where the band gap in semiconductors is underestimated. To amend this, we shift the conduction (valence) bands upward (downwards) by adding (subtracting) orbital-dependent potentials into the Hamiltonian as a standard procedure [32, 33] and reproduce the experimental band gap [31].

The results for the partial densities of states (PDOS) and band dispersions thus obtained are shown in Fig. 1. We find that the system is a direct-gap semiconductor with the gap minimum at the Γ -point of the Brillouin zone in agreement with experiment [24, 27]. The band structure near the Fermi level is rather simple; the conduction band has a cosine-like quasi-1D band dispersion coming from the $5d_{xy}$ orbitals of Ta ions arranged along the chain, whereas the top of the valence band has a quasi-1D dispersion coming from the Ni $3d_{xz+yz}$ and Se $4p_{x+y}$ orbitals arranged along the chain, and no hybridization occurs between the top of the valence band and bottom of the conduction band.

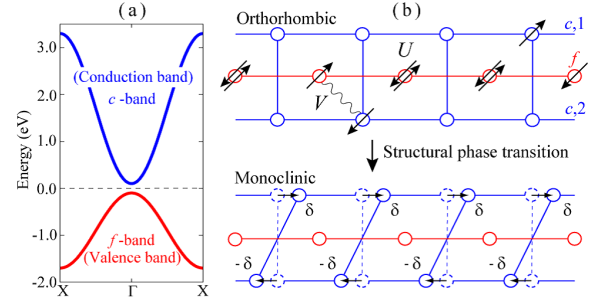


FIG. 2: (Color online) (a) Noninteracting band dispersion of our model Eq. (1). The conduction band is doubly degenerate. (b) Schematic representations of the three-chain Hubbard model for the 1D structural unit consisting of the two chains of the Ta $5d_{xy}$ orbitals yielding the c -bands and one chain of the Ni $3d_{xz+yz}$ and Se $4p_{x+y}$ orbitals of Ta_2NiSe_5 yielding the f -band. The lattice distortion of the chain corresponding to the orthorhombic-to-monoclinic phase transition is schematically illustrated.

Based on the results, we make the effective three-chain model containing the valence f -band coming from the hybridized Ni $3d_{xz+yz}$ and Se $4p_{x+y}$ orbitals and the doubly degenerate conduction c -bands coming from the Ta $5d_{xy}$ orbitals, to which the Hubbard-type onsite (U_c and U_f) and interchain (V) repulsive interactions are added (see

Fig. 2). We also introduce the electron-phonon interaction with strength g and the phonon term with phonon frequency ω_c assuming a uniform shear distortion of the chain (see Fig. 2) corresponding to the structural transition from the orthorhombic to monoclinic phase [31, 34]. The Hamiltonian reads

$$\begin{aligned} \mathcal{H} = & \sum_{k,\sigma,\alpha} \varepsilon_c(k) c_{k,\sigma,\alpha}^\dagger c_{k,\sigma,\alpha} + \sum_{k,\sigma} \varepsilon_f(k) f_{k,\sigma}^\dagger f_{k,\sigma} \\ & + U_c \sum_{i,\sigma,\alpha} n_{i,\uparrow,\alpha}^c n_{i,\downarrow,\alpha}^c + U_f \sum_{i,\sigma} n_{i,\uparrow}^f n_{i,\downarrow}^f \\ & + V \sum_{i,\sigma,\sigma',\alpha} (n_{i,\sigma,\alpha}^c + n_{i+1,\sigma,\alpha}^c) n_{i,\sigma'}^f \\ & + \frac{g}{\sqrt{L}} \sum_{k,q,\sigma,\alpha} \left[(b_{q,\alpha} + b_{-q,\alpha}^\dagger) c_{k+q,\sigma,\alpha}^\dagger f_{k,\sigma} + \text{H.c.} \right] \\ & + \omega_c \sum_{q,\alpha} b_{q,\alpha}^\dagger b_{q,\alpha} \end{aligned} \quad (1)$$

where $c_{k,\sigma,\alpha}^\dagger$ and $f_{k,\sigma}^\dagger$ are the Fourier transforms of $c_{i,\sigma,\alpha}^\dagger$ that creates an electron with spin σ ($=\uparrow, \downarrow$) at site i on the c -orbital of the chain α ($=1, 2$) and $f_{i,\sigma}^\dagger$ that creates an electron at site i of the f -orbital, respectively. $n_{i,\sigma,\alpha}^c$ and $n_{i,\sigma}^f$ are the electron number operators on the c - and f -orbitals, respectively. The noninteracting band dispersions are given as $\varepsilon_c(k) = 2t_c(\cos k - 1) + D/2 - \mu$ and $\varepsilon_f(k) = 2t_f(\cos k - 1) - D/2 - \mu$ with the hopping parameters t_c and t_f and the band gap D . We use the values $t_c = -0.8$, $t_f = 0.4$, and $D = 0.2$ in units of eV obtained from the fitting to the calculated band dispersion (see Fig. 1). μ is the chemical potential. We assume $U_c = U_f (=U)$ for simplicity and choose $V = U/4$. The bosonic operator $b_{q,\alpha}^\dagger$ creates a phonon with momentum q in the chain α . L is the number of the unit cell, where the unit cell contains an f - and two c -orbitals. We restrict ourselves to the filling of two electrons per unit cell.

We apply the mean-field approximation $n_{i,\uparrow} n_{i,\downarrow} \rightarrow \langle n_{i,\uparrow} \rangle n_{i,\downarrow} + n_{i,\uparrow} \langle n_{i,\downarrow} \rangle$ for the onsite terms of both c - and f -orbitals and $n_{i,\sigma,\alpha}^c n_{j,\sigma}^f \rightarrow \langle n_{i,\sigma,\alpha}^c \rangle n_{j,\sigma}^f + n_{i,\sigma,\alpha}^c \langle n_{j,\sigma}^f \rangle - \langle f_{j,\sigma}^\dagger c_{i,\sigma,\alpha} \rangle c_{i,\sigma,\alpha}^\dagger f_{j,\sigma} - f_{j,\sigma}^\dagger c_{i,\sigma,\alpha} \langle c_{i,\sigma,\alpha}^\dagger f_{j,\sigma} \rangle$ for the inter-chain term. We define the order parameter for the spin-singlet excitons as $\Delta_\alpha = |\Delta| e^{i\theta_\alpha} = \frac{V}{2L} \sum_{k,\sigma} \langle c_{k,\sigma,\alpha}^\dagger f_{k,\sigma} \rangle$, excluding possibility of the formation of any density waves because the top of the valence band and bottom of the conduction band are both at the Γ -point of the Brillouin zone [4]. Accordingly, the order parameter for the uniform lattice distortion is defined as $\delta_\alpha = 2g\langle b_{q=0,\alpha} \rangle / \sqrt{L}$ with $\langle b_{q,\alpha} \rangle \neq 0$ only at $q = 0$, whereby the shear distortion of the chain corresponding to the structural transition from the orthorhombic to monoclinic phase can be described by $|\delta|$ with $\delta_1 = |\delta|$ and $\delta_2 = -|\delta|$. We use a parameter $\lambda = g^2/\omega_c$ in the following discussions. We define n to be $n = \langle n_{i,\sigma,\alpha}^c \rangle$ and $1 - 2n = \langle n_{i,\sigma}^f \rangle$, which is a measure of the spontaneous c - f hybridization at $T = 0$ K. Following the standard

procedure of the mean-field theory [31], we derive the mean-field Hamiltonian and diagonalize it by the Bogoliubov transformation. The self-consistent (or gap) equations are derived by the minimization of the free energy, which are solved numerically to obtain the temperature dependence of n , $|\delta|$, and $|\Delta|$.

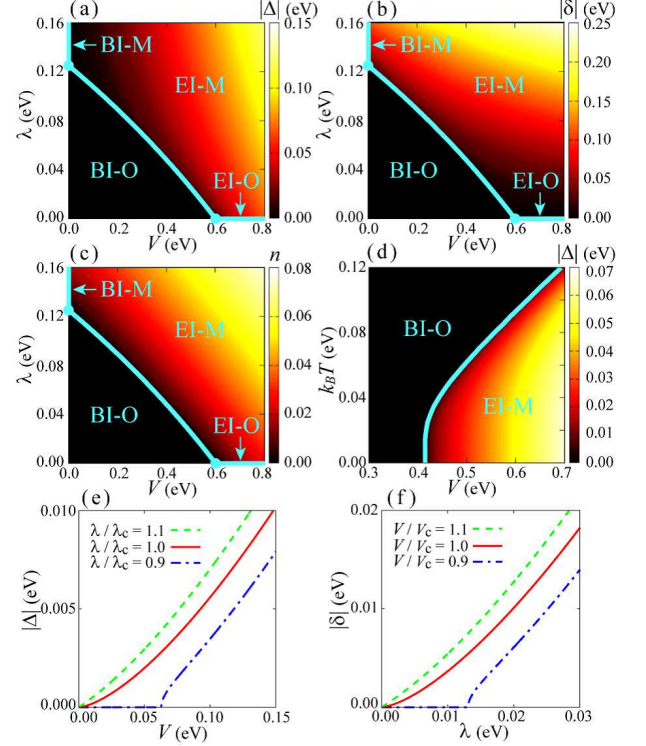


FIG. 3: (Color online) Ground-state phase diagram with the order parameters (a) $|\Delta|$, (b) $|\delta|$, and (c) n , in the parameter space (V, λ) . (d) Finite-temperature phase diagram with the order parameter $|\Delta|$ as a function of V at $\lambda = 0.04$ eV. Also shown are (e) the V dependence of $|\Delta|$ and (f) λ dependence of $|\delta|$ at $T = 0$ K with $\lambda_c = 0.125$ eV and $V_c = 0.6$ eV. Abbreviations are BI (band insulator), EI (excitonic insulator), O (orthorhombic), and M (monoclinic).

The calculated results for the ground-state and finite-temperature phase diagrams are shown in Fig. 3. As for the ground state, we clearly see in Figs. 3 (a)-(c) that when V and λ are small the system is the band insulator (BI) with $|\Delta| = |\delta| = 0$ but when V and λ are large the EI state $|\Delta| > 0$ with the shear distortion of the chain $|\delta| > 0$ appears in the ground state. The EI state occurs simultaneously and cooperatively with the lattice distortion except at the lines $\lambda = 0$ and $V = 0$. We emphasize here that even if λ is small the structural phase transition occurs with help of the exciton condensation: i.e., the interaction V drives the EI-state formation $\Delta > 0$, which leads to the spontaneous c - f hybridization, and as a consequence, the structural distortion $\delta > 0$ occurs even if λ is small. The spontaneous c - f hybridization stabilizes the lattice distortion, leading to the orthorhombic-

to-monoclinic phase transition. This is consistent with the situation in the real material Ta_2NiSe_5 , where the monoclinic distortion of the angle $0.5^\circ - 1^\circ$ (or the atomic displacement $0.02 - 0.04 \text{ \AA}$) is very small [26, 27]; a rough estimation may be $|\delta| \sim 0.02 - 0.04 \text{ eV}$, which corresponds to $\lambda \sim 0.02 - 0.05 \text{ eV}$ [31]. The oxidation states of Ni^{2+} and Ta^{4+} observed in the XPS experiment [24] are also consistent with the nonzero value of n induced by the spontaneous c - f hybridization in the EI phase (see Fig. 3(c)).

The temperature dependence of the EI phase is given in Fig. 3(d), where we find that by lowering temperature the BI state with the undistorted (orthorhombic) structure changes into the EI state with the distorted (monoclinic) structure and the transition is of the second order. Thus, the experimental situations are correctly reproduced. We also point out that the observed sudden drop in the uniform magnetic susceptibility at the transition [27] may be due to the formation of spin-singlet excitons that suppresses the paramagnetic part of the uniform spin susceptibility of thermally activated electrons.

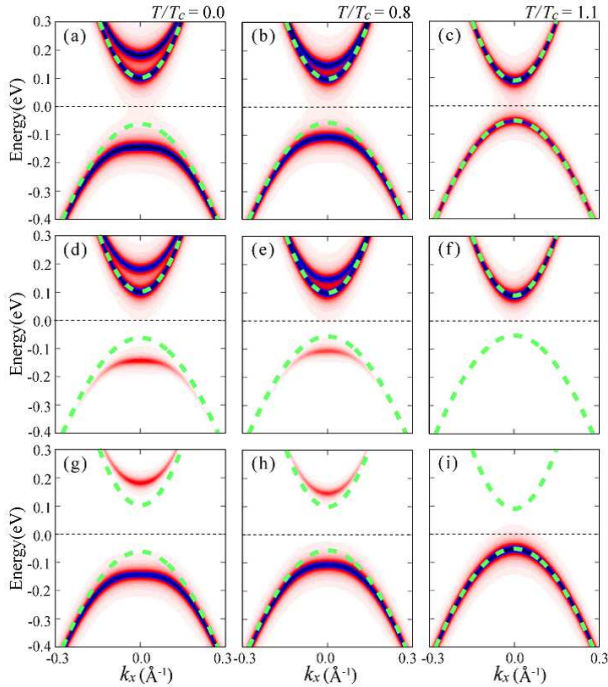


FIG. 4: (Color online) Calculated temperature dependence of the single-particle spectra of the three-chain Hubbard model. (a)-(c): Total spectral weight, (d)-(f): spectral weight on the c -orbital, and (g)-(i): spectral weight on the f -orbital. We assume $V = 0.55 \text{ eV}$ and $\lambda = 0.04 \text{ eV}$. The calculated transition temperature is $k_B T_c = 0.0783 \text{ eV}$. The Lorentzian broadening of the spectra of 0.01 eV is applied for comparison with the experimental ARPES spectra [24, 25]. The band dispersion without condensation $|\Delta| = |\delta| = 0$ is given by the dashed curves. The Fermi level is indicated by a horizontal line.

The calculated temperature dependence of the single-particle spectra is shown in Fig. 4, where we find the large deformation of the top of the valence band caused by the spontaneous c - f hybridization in the EI state formation by lowering temperature: the flattening of the band dispersion is evident and the shift of the top of the valence band away from the Fermi level is noticed, both of which are consistent with experimental ARPES results [24, 25]. The hybridization can be seen in the c -orbital spectral weight *below* the Fermi level (see Figs. 4 (d) and (e)) and f -orbital spectral weight *above* the Fermi level (see Figs. 4 (g) and (h)). Splitting of the c -bands into two is also noticed, where the lower “nonbonding” band remains unaffected in the presence of $|\Delta|$ and $|\delta|$. Note that the c - f hybridization is absent above the transition temperature (T_c) in our mean-field calculations (see Figs. 4 (c), (f), and (i)). However, the characteristic temperature scale associated with the formation of preformed excitons should be present [5], which we hope will be observed in any future experiment.

In summary, we have discussed the origin of the orthorhombic-to-monoclinic phase transition of the layered dichalcogenide Ta_2NiSe_5 using the band structure calculation and mean-field analysis of the derived three-chain Hubbard model. We have shown that the BEC of excitonic electron-hole pairs cooperatively induces the instability of the phonon mode at momentum $q \rightarrow 0$ in the quasi-1D Ta-NiSe-Ta chain, resulting in the structural phase transition of the system. We have also shown that the spontaneous c - f hybridization explains the valence states of Ni and Ta ions observed in the XPS experiment and that the calculated single-particle spectra reproduce the flattening and shift of the band structure observed in the ARPES experiment. All of these results support the EI state formation due to the BEC mechanism of spin-singlet excitons for the intriguing phase transition observed in Ta_2NiSe_5 .

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